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BARTELLS

On a Hydrazine Derivative  
Of Ethyl Dihydroxymalonate  
And some of its Reactions

Chemistry

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ON A HYDRAZINE DERIVATIVE OF  
ETHYL DIHYDROXYMALONATE AND SOME OF  
ITS REACTIONS

BY

EDWIN J. BARTELLS

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THESIS

For the Degree of Bachelor of Science


in Chemistry

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College of Science

University of Illinois

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PRESENTED JUNE, 1908 





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UNIVERSITY OF ILLINOIS

May 29, 1908

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Edwin J. Bartells

ENTITLED On a Hydrazine Derivative of Ethyl Dihydroxymalonate  
and Some of its Reactions

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemistry

Richard A. Curtis

Instructor in Charge.

APPROVED:

W. A. Noyes

HEAD OF DEPARTMENT OF

114561

Chemistry





ON (A (HYDRAZINE) DERIVATIVE  
OF ETHYL DIHYDROXYMALONATE AND  
SOME OF ITS REACTIONS

by

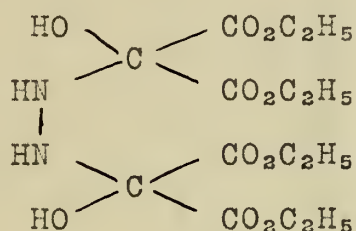
EDWIN J. BARTELLS



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In his work on "The Reaction of Hydrazine on Ethyldihydroxymalonate," Koch<sup>1</sup> used a solution of hydrazine hydrate and obtained a crystalline hydrazine derivative of this ester. We have studied the reactions of this substance, with a view of determining whether or not it is a symmetrical hydrazine derivative:-



We have also improved the method of preparing it so that we get a good yield and a greater degree of purity.

#### Preparation of the Hydrazine Derivative.

5.3 g. of sodium carbonate (anhydrous) were added to 6.5 g. of hydrazine sulphate in 30 cc. of water. This solution was slowly added to 19.2 g. of the ester in 10 cc. of water.

The solution became turbid by the separation of a light oil and carbon dioxide was evolved until about one-half of the hydrazine solution had been added. When the reaction was complete the oily product was crystallized by vigorous rubbing with a glass rod. If the crystallization is very fine the product can be easily purified by washing until perfectly white with cold water, in which it is slightly soluble. The filtrate may be extracted with ether and the yield somewhat increased. This product melted at 58°, was identical with that prepared from hydrazine hydrate and corresponded to the following empir-

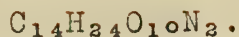
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1) Thesis, U. of I., '07. P. 4.

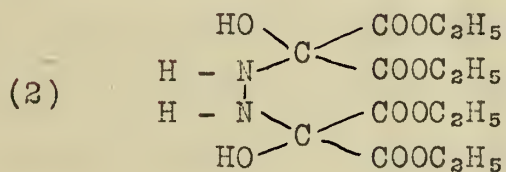
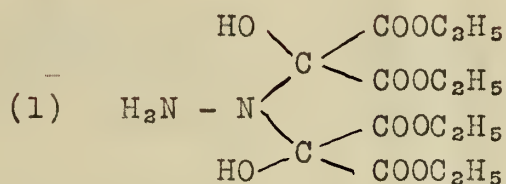




ical formula:-



In order to determine which of the following formulas:-



is the correct one for this substance we have continued Koch's study of its reactions with benzaldehyde, phosphorous pentoxide and benzoyl chloride and in addition the action of mercuric oxide and benzoic anhydride.

#### Action of Mercuric Oxide on the Hydrazine Derivative.

To ascertain if an azotartronic ester,  $\begin{array}{c} \text{C}_2\text{H}_5\text{OOC} \quad \text{COOC}_2\text{H}_5 \\ \diagdown \quad \diagup \\ \text{C} - \text{N} = \text{N} - \text{C} \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$ ,

could be produced by removing the two remaining hydrazine hydrogen atoms the following oxidation test was made. To 3 g. of the hydrazine derivative dissolved in 12 cc. of benzene we added 1.705 (one molecule) of mercuric oxide, and gently heated. The solution darkened, metallic mercury separated out and nitrogen gas was evolved at 25°-30°. The temperature was raised to 60° and at the end of an hour about three-fourths of the nitrogen present in the substance, had been evolved. It was collected in an



azotometer over a potash solution, the air having been displaced in the apparatus by carbon dioxide at the start. An additional 1.705 g. of mercuric oxide, one molecule, increased the volume of gas in the azotometer about one-third.

Calculated for  
 $C_{14}H_{24}O_{10}N_2$

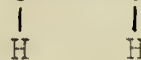
Found

N = 7.36 o/o = 6.86 o/o

Mercuric oxide remained in excess. The contents of the flask were filtered and from the filtrate a white crystalline substance was obtained having a melting point of 57°-57.5° and identical in properties with ethyl dihydroxymalonate. The hydrazine radical was therefore oxidized to water and nitrogen, regenerating ethyl dihydroxymalonate.

#### Action of Benzaldehyde on the Hydrazine Derivative.

When benzaldehyde and the hydrazine derivative were mixed in the molecular ratios of 1 : 1 or 2 : 1 there was no apparent reaction in the cold. When in either case, however, absolute methyl alcohol was added clusters of radiating crystals appeared in a few minutes. These crystals are yellow, melt at 93° and are identical with benzalazin,  $C_6H_5-C=N-N=C-C_6H_5$ ,



first made by Curtius<sup>1</sup>. Hydrazine is therefore dissociated and reacts with the benzaldehyde to form the azine body. It is impossible to determine whether or not this dissociation precedes the initial action of the benzaldehyde.

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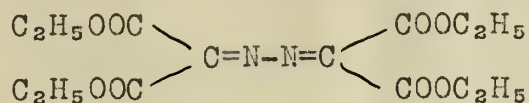
1) J. f. prak. Chem. (2) 39, p. 44.





Action of Phosphorous Pentoxide on the  
Hydrazine Derivative.

To ascertain if the two hydroxyl groups could be withdrawn as water, to form an azinemalonic ester,



phosphorous pentoxide was added to the hydrazine derivative in the ratio of two molecules of the former to three of the latter, no solvent being used. The mixture, in a tightly stoppered flask, was allowed to stand twenty-four hours. The mass slowly changed to a yellow, honey-like oil. If warmed slightly the action is much more rapid. Attempts were made to purify the product as follows:- The oil was separated from the phosphoric acid by extracting with ether. The washed ethereal solution was dried over calcium chloride and concentrated leaving a thick yellow oil. This oil decomposed entirely when distilled in a vacuum, yielding tarry products.

An attempt to obtain a pure product by distilling a mixture of the theoretic quantities of phosphorous pentoxide and hydrazine derivative in a vacuum resulted likewise in destructive decomposition. The following tests were applied to the crude yellow oil from the ether extract.

(a) To 1.72 g. of oil in 2 cc. of absolute alcohol were added 2 cc. (one molecule) of a saturated alcoholic potash solution and the vessel placed in a freezing mixture for a few minutes and then warmed up to 25°. A small amount of yellow gummy salt was precipitated after ten or twelve minutes, and



a small amount of gas was evolved. After diluting and boiling the solution white crystals were formed. These crystals were extracted with ether and melted at 95°. They are fairly soluble in absolute alcohol, easily soluble in ether and crystallize from this solvent in asbestos-like fibres one inch long. The yield was small and this was not further studied.

(b) 1. Concentrated ammonium hydroxide gives with the oil a lot of fine, pale yellow, thistle-like balls of crystals. 2. The oil when boiled with concentrated ammonium hydroxide and absolute alcohol gave a white, crystalline precipitate. On standing the solution passed through red to magenta, probably due to saponification and an amid formation. 3. When dry ammonia gas is passed into a benzene solution of the oil a small amount of a white, floccy mass precipitates.

(c) Sodium in dry ether reacts with the oil evolving a gas and forming a small amount of a pale yellow salt soluble in acetone and water.

(d) Reduced with sodium amalgam a small quantity of a white, crystalline body is found together with a large quantity of ammonia gas.

In all these tests the yields of clean products were too small to be advantageously studied further.

#### Action of Benzoyl Chloride on the Hydrazine Derivative.

In order to show the exact hydrazine structure of this body the following attempts were made to prepare the benzoyl derivative. 5.0 g. of the hydrazine derivative were dissolved in 60 cc. of ether and to this solution was added 2.8 g. of





sodium carbonate (anhydrous) dissolved in 15 cc. of water. 7.4 g. of benzoyl chloride were added to the above mixture, drop by drop. A precipitation of crystals began after a minute or so. After standing several hours the white, curdy mass was washed with water in a separatory funnel. The crystals washed with ether weighed 2.1 g. and melted at  $241^{\circ}$ - $241.5^{\circ}$  (corr.) after being recrystallized twice from 95 % alcohol.

We substituted first pyridine, then sodium hydrate, for the sodium carbonate in this reaction but with like results. Acetic anhydride with the pyridine did not materially affect the reaction.

This product resembles asbestos fibre when wet; the powdered substance is chalky in appearance. It is almost insoluble in cold water, chloroform, alcohol and ether. It is fairly soluble in hot 95 % alcohol from which it is precipitated by cold water.

Analysis of this substance gave the following results:-

- I. 0.1981 g. substance gave 20.9 cc. N at  $24^{\circ}$  and 751.4 mm.
- II. 0.2073 g. substance gave 22.0 cc. N at  $25.5^{\circ}$  and 753 mm.
- III. 0.3842 g. substance gave 0.9859 g.  $\text{CO}_2$  and 0.1814 g.  $\text{H}_2\text{O}$ .
- IV. 0.3220 g. substance gave 0.8256 g.  $\text{CO}_2$  and 0.1516 g.  $\text{H}_2\text{O}$ .

Calculated for  $\begin{array}{c} \text{C}_6\text{H}_5\text{CO}-\text{N}-\text{H} \\ | \\ \text{C}_6\text{H}_5\text{CO}-\text{N}-\text{H} \end{array}$

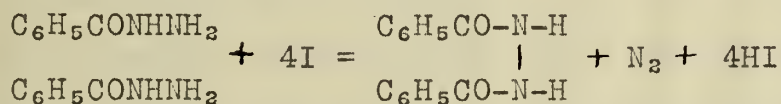
	Theory	Found			
		I	II	III	IV
N	11.66	12.04	12.07		
C	70.			69.98	69.92
H	5.			5.24	5.22



Benzoic Anhydride on the Hydrazine Derivative  
in Absolute Ether Solution.

In order to find out if dibenzoyl hydrazine could be formed in this reaction in the absence of water, which might have acted as a saponifying agent in these experiments, the following test was made. 2 g. of the hydrazine derivative and 2.4 g. of benzoic anhydride, two molecules, were dissolved in absolute ether, freshly distilled over sodium and the flask tightly closed. After standing two hours white fibrous crystals began to separate out slowly. 0.5 g. was thus obtained after the mixture had stood several days. This product appears identical with the one prepared from benzoyl chloride and the hydrazine derivative. In wet ether the reaction goes much faster but gives the same product.

Curtius<sup>1</sup> prepared the symmetrical dibenzoyl hydrazine by oxidizing benzhydrazid with iodine:



Our benzoyl derivative has the same characteristic appearance and relative solubilities as the substance thus formed by Curtius. It differs, however, in its melting point, which is 8° higher (241° corr.) than he found it.

A product identical with ours was prepared by Curtiss and Tarnoski<sup>2</sup> from the hydrazine derivative of methyl dihydroxy-malonate and benzoyl chloride.

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1) Curtius, J. f. prak. Chem. (2) 50, 299.

2) Tarnoski Thesis, U. of I., '07.









In addition to these studies of the hydrazine derivative of ethyl dihydroxymalonate we have made tests of the action of hydroxylamine on ethyl dihydroxymalonate and also tests on the acid oils remaining in the distillate from which the ethyl dihydroxymalonate crystals were formed.<sup>1</sup>

Action of Hydroxylamine on Ethyl Dihydroxymalonate.

9.6 g. of ethyl dihydroxymalonate were added to a solution containing 3.48 g. of hydroxylaminehydrochloride, one molecule, and 2.6 g. of sodium carbonate in 10 cc. of water. There was no lowering in temperature, as is the case when the ester dissolves alone; hence, a reaction was indicated. When heated to about 100° an oil began to separate out on top which, when cool, settled to the bottom. The oil was extracted with ether, washed with water, and the ether dried with calcium chloride, evaporated. This oil is colorless, has no odor and is of a glycerine-like consistency. It boils at about 150° with decomposition.

The following tests were made on the oil:

(a) Aqueous potassium hydroxide gives a yellow solution with the generation of much heat. On adding absolute alcohol to this and heating an evolution of gas takes place.

(b) Alcoholic potash gives a yellow salt at once which on the addition of absolute alcohol turns to a white gum.

(c) Silver nitrate is apparently without action on the oil but on adding ammonia a yellowish white salt precipitates and dissolves in an excess. On warming this solution a heavy reduction of silver takes place, <sup>and</sup> the solution turns green. A sim-

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1) Curtiss, Amer. Ch. Journ. 35,477 (1906).





ilar behavior has been noticed with the corresponding product from the methyl ester.<sup>1</sup>

(d) Sodium in dry ether gives an intense frothing, apparently hydrogen gas. The solution becomes yellow and a yellow salt of sodium separates out which redissolves in the course of three hours. On evaporation of the ether a yellow resin is left which becomes semi-liquid in the air. Silver nitrate on this gum gives a yellow salt soluble in an excess of water.

On the Acid Oils from the Mother Liquors in  
Preparing Ethyl Dihydroxymalonate.

When ethyl dihydroxymalonate is prepared by passing nitrous anhydride into ethyl malonate<sup>2</sup> there remains in the mother liquor from the mesoxalic crystals, oils having acid properties and containing nitrogen. From these oils a yellow potassium salt was prepared.<sup>3</sup>

We have freed the acid from this salt and made some study of its reaction with hydrazine.

A solution of hydrazine carbonate was added slowly to some of the purified<sup>acid</sup> oil dissolved in absolute alcohol. Some heat was generated, a large amount of gas was evolved, the solution turned red and a yellow salt which precipitated out was filtered off. This salt was extracted with 95 % alcohol leaving a white residue. The alcoholic extract was evaporated nearly to dryness on a water bath. The crystals which separated out were

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1) Tarnoski Thesis, U. of I., 1907.

2) Amer. Chem. Journ. 35, 477.

3) Amer. Chem. Journ. 35, 483.



washed with ether several times to remove the yellow oil and twice recrystallized from 3 - 4 volumes of hot absolute alcohol in which they are very soluble. From this solution the substance crystallized in bunches of needles or prisms apparently monoclinic. These crystals are canary yellow and are insoluble in ether. When placed in a melting-point flask a slight darkening in color occurs at about 100° and gaseous decomposition sets in at about 111° the substance changing to a yellow liquid. When this yellow liquid cools it recrystallizes and remelts with gaseous decomposition at about 85°-95°, apparently a new substance.

Analysis:

Calculated for  $C_5H_{12}O_5N_4$

	Theory	Found	
N	26.92	30.26	28.26

Owing to the explosive decomposition of this substance when heated satisfactory figures have not yet been obtained.

The potassium salt of this acid oil, which is being studied in this laboratory at the present time, appears to have a structure analogous to the hydrazine salt.

A very explosive crystalline substance was obtained from the alcoholic mother liquor of the above hydrazine salt which was analyzed. These crystals melt at about 95° to a dark red liquid with gaseous decomposition. The substance crystallizes in yellow, thistle-like balls or like paper fibre and is difficultly soluble in absolute alcohol.





These acid oils and their salts are now being thoroughly investigated in this laboratory.

Laboratory of Organic Chemistry

University of Illinois.

Edwin J. Bartells

in conjunction  
with

April 15, 1908.

Dr. R. S. Curtiss







UNIVERSITY OF ILLINOIS-URBANA



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